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$\text{Ag}_{2.54}\text{Tl}_2\text{Mo}_{12}\text{Se}_{15}$: a new structure type containing Mo_6 and Mo_9 clusters

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The novel structure-type $\text{Ag}_{2.54}\text{Tl}_2\text{Mo}_{12}\text{Se}_{15}$ (silver thallium molybdenum selenide) is built up of $\text{Mo}_6\text{Se}_8\text{Se}_6^{\text{a}}$ and $\text{Mo}_9\text{Se}_{11}\text{Se}_6^{\text{a}}$ cluster units in a 1:2 ratio, which are three-dimensionally connected to form the Mo–Se network. The Ag and Tl cations are distributed in several voids within the cluster network. Three of the seven independent Se atoms and one Tl atom lie on sites with $\bar{3}$ symmetry (Wyckoff sites $2c$ or $2d$).

Comment

In solid-state chemistry, the crystal structures of reduced molybdenum chalcogenides are characterized by molybdenum clusters of various sizes and geometries. Although most Mo cluster compounds contain just one type of cluster, some of them can present up to four different types, as observed in $\text{Pr}_4\text{Mo}_9\text{O}_{18}$ (Tortelier & Gougeon, 1998). In most reduced Mo chalcogenides, we have observed only one type of cluster, as exemplified by the series $M_{n-2}\text{Mo}_{3n}\text{X}_{3n+2}$ ($M = \text{Rb}$ or Cs ; $X = \text{S}$, Se or Te ; $n = 3, 4, 5, 6, 7, 8, 10$ or 12) containing Mo_9 , Mo_{12} , Mo_{15} , Mo_{18} , Mo_{21} , Mo_{24} , Mo_{30} and Mo_{36} clusters (Gautier *et al.*, 1998; Gougeon, 1984; Gougeon *et al.*, 1984, 1987, 1988, 1989*a,b*, 1990; Thomas *et al.*, 1997; Picard, Gougeon & Potel, 1999; Picard, Halet *et al.*, 1999). On the other hand, in the series $\text{Rb}_{2n}\text{Mo}_9\text{X}_{11}\text{Mo}_{6n}\text{X}_{6n+2}$ ($n = 1, 2, 3, 4$ and 5 ; Picard *et al.*, 2000), we found clusters of odd and even nuclearity which co-exist in equal proportions. Subsequently, we presented a new structural type, $\text{Rb}_4\text{Mo}_{21}\text{Se}_{24}$ (Picard *et al.*, 2001), also containing odd and even nuclearity clusters, *i.e.* Mo_{12} and Mo_{15} , but in the ratio 1:2. We report here a new structural type, $\text{Ag}_{2.54}\text{Tl}_2\text{Mo}_{12}\text{Se}_{15}$, containing Mo_6 and Mo_9 clusters in the ratio 1:2.

A view of the crystal structure of $\text{Ag}_{2.54}\text{Tl}_2\text{Mo}_{12}\text{Se}_{15}$ is shown in Fig. 1. It is based on octahedral Mo_6 and bioctahedral Mo_9 clusters surrounded by 14 and 17 Se atoms, respectively (Fig. 2), to form $\text{Mo}_6\text{Se}_8\text{Se}_6^{\text{a}}$ and $\text{Mo}_9\text{Se}_{11}\text{Se}_6^{\text{a}}$ cluster units. The latter units share some of their Se ligands according to the

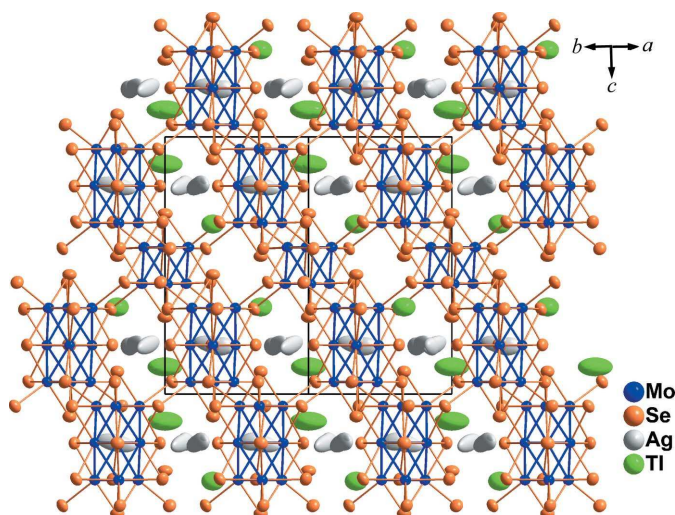


Figure 1

A view of $\text{Ag}_{2.54}\text{Tl}_2\text{Mo}_{12}\text{Se}_{15}$ along $[110]$. Displacement ellipsoids are drawn at the 97% probability level.

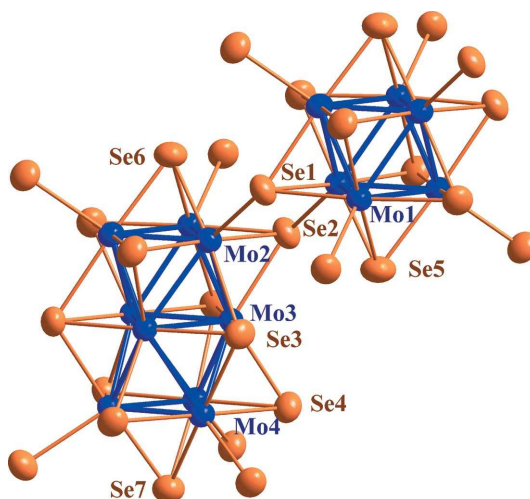


Figure 2

Plot showing the atom-numbering scheme and the inter-unit linkage of the $\text{Mo}_9\text{Se}_{11}\text{Se}_6$ and $\text{Mo}_6\text{Se}_8\text{Se}_6$ cluster units. Displacement ellipsoids are drawn at the 97% probability level.

connective formulae $\text{Mo}_6\text{Se}_2\text{Se}_{6/2}^{\text{i-a}}\text{Se}_{6/2}^{\text{a-i}}$ and $\text{Mo}_9\text{Se}_5\text{Se}_{6/2}^{\text{i-a}}\text{Se}_{6/2}^{\text{a-i}}$ to form the three-dimensional Mo–Se framework [for details of the i- and a-type (*inner* and *ausser*) ligand notation, see Schäfer & von Schnering (1964)]. This arrangement results in each $\text{Mo}_6\text{Se}_8\text{Se}_6$ unit being surrounded by six $\text{Mo}_9\text{Se}_{11}\text{Se}_6$ units centred at the apices of a trigonal prism, while each $\text{Mo}_9\text{Se}_{11}\text{Se}_6$ unit is surrounded by three $\text{Mo}_6\text{Se}_8\text{Se}_6$ and three $\text{Mo}_9\text{Se}_{11}\text{Se}_6$ units, also forming a trigonal prism.

The Mo_6 cluster exhibits $\bar{3}$ symmetry, as in the rhombohedral Chevrel phase $M_x\text{Mo}_6\text{Se}_8$. The Mo_6 cluster is slightly distorted, with Mo–Mo distances of 2.6879 (10) Å for the intra-triangle distances (distances between the Mo atoms related through the threefold axis) and 2.7007 (7) Å for the inter-triangle distances. This clearly indicates that the number of electrons per Mo_6 , also called the metallic electron count (MEC), should be close to 23. Indeed, previous work on the

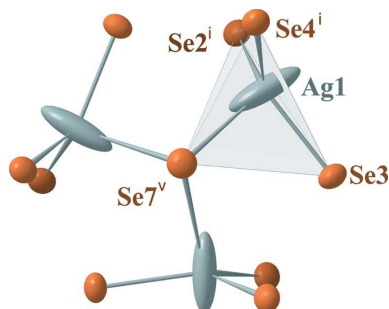


Figure 3
The Se coordination polyhedron for Ag1. The symmetry codes are as in Table 1.

Chevrel phases (Yvon *et al.*, 1977) has shown that when the MEC increases from 20 to 24, the Mo_6 cluster becomes more regular. Thus, in Mo_6Se_8 in which the MEC is 20, the intra- and inter-triangle Mo—Mo distances are 2.683 and 2.836 (8) Å, respectively (Bars *et al.*, 1973), while in $\text{Pr}_{0.86}\text{Mo}_6\text{Se}_8$ (Le Berre *et al.*, 2000), with an MEC of 22.58, the intra- and inter-triangle Mo—Mo distances are 2.6812 (6) and 2.7268 (7) Å, respectively, and in $\text{Li}_{3.2}\text{Mo}_6\text{Se}_8$, with an MEC of 23.2, they are 2.6727 and 2.6733 Å, respectively (Cava *et al.*, 1984).

The Mo_9 cluster exhibits 3.. symmetry. The Mo—Mo distances within the Mo_9 clusters are 2.6374 (8), 2.7346 (7) and 2.6163 (9) Å within the triangles made by atoms Mo2, Mo3 and Mo4, respectively, 2.6896 (8) and 2.7757 (7) Å for the inter-triangle distances between the two triangles formed by atoms Mo2 and Mo3, respectively, and 2.6628 (8) and 2.7475 (8) Å for the the inter-triangle distances between the two triangles formed by atoms Mo3 and Mo4, respectively.

In the Mo_9 cluster, the MEC, which can vary from 32 to 36 (Hughbanks & Hoffmann, 1983; Gautier *et al.*, 1997), predominantly affects the Mo—Mo bonds within the median triangle ($\text{Mo3}—\text{Mo3}^{\text{iii}}$ bonds in the title compound; symmetry codes are as in Table 1) (Potel *et al.*, 1984). A comparison of the Mo—Mo bonds within the median triangle in different compounds containing only Mo_9 clusters shows they are similar in the title compound [2.7346 (7) Å] and in $\text{Ag}_{4.1}\text{Cl-Mo}_9\text{Se}_{11}$ [2.7362 (5) Å], in which the MEC is 35.1 (Gougeon *et al.*, 2004). Consequently, the approximately nine electrons contributed by the five Ag and four Tl atoms are distributed uniformly over the Mo_6 and the two Mo_9 clusters contained in the unit cell (about three electrons on each cluster). The average Mo—Mo distances in the two clusters are very similar, 2.693 Å in the Mo_6 cluster and 2.694 Å in the Mo_9 cluster. The shortest inter-cluster Mo—Mo distances are 3.6041 (11) Å between the Mo_6 and Mo_9 clusters, and 3.6725 (9) Å between the Mo_9 clusters. The Se atoms bridge either one or two Mo triangular faces of the clusters. Moreover, atoms Se1 and Se2 are linked to an Mo atom of a neighbouring cluster. The Mo—Se bond distances range from 2.5492 (9) to 2.6457 (11) Å within the $\text{Mo}_6\text{Se}_8\text{Se}_6$ unit and from 2.5319 (9) to 2.7085 (10) Å within the $\text{Mo}_9\text{Se}_{11}\text{Se}_6$ unit.

The Ag and Tl atoms reside in cavities between the cluster units. Atom Ag1 partially occupies [0.845 (3)] triangular groups of distorted tetrahedral sites of Se atoms having the

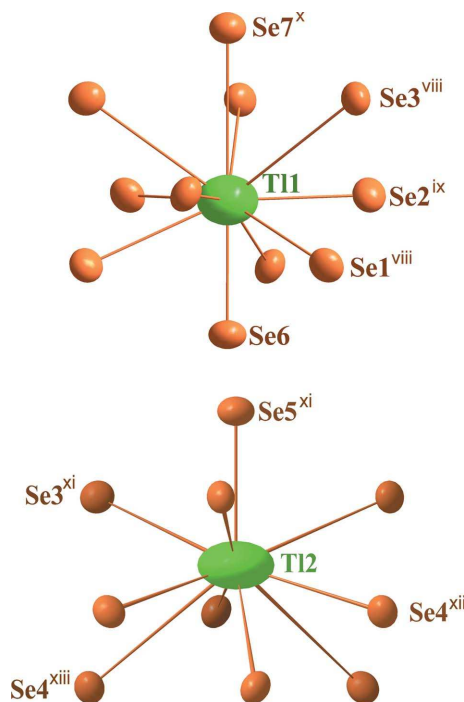


Figure 4
The environments of atoms Tl1 and Tl2. The symmetry codes are as in Table 1.

apex atom Se7 in common around the threefold axis (Fig. 3). The maximum of the Ag1 probability density function is very close to the triangular face opposite the common apex atom Se7, with Ag1—Se distances of 2.577 (2), 2.6675 (17) and 2.6834 (16) Å, the Ag1—Se7^v distance being 3.0215 (17) Å. The Tl1 and Tl2 cations are in penta- and tetracapped trigonal prismatic environments of Se atoms (Fig. 4); the former is similar to that observed for the *M* element in the ternary compounds $\text{M}_2\text{Mo}_{15}\text{Se}_{19}$ (*M* = In and Ba), in which Mo_6 and Mo_9 clusters co-exist in equal proportions (Potel *et al.*, 1981; Gougeon *et al.*, 1989c). The Tl—Se distances range from 3.0677 (14) to 4.2039 (9) Å for the Tl1 site.

It is interesting to note that, while in $\text{Ba}_2\text{Mo}_{15}\text{Se}_{19}$ the Ba atom is nearly equidistant from the axial atoms Se6 and Se7 [3.4689 (5) and 3.4761 (5) Å, respectively], in $\text{Ag}_{2.54}\text{Tl}_2\text{-Mo}_{12}\text{Se}_{15}$ atom Tl1 is displaced towards the axial atom Se6, with a Tl1—Se6 distance of 3.0677 (14) Å compared with 3.8863 (14) Å for Tl1—Se7^x. This effect, which may result from the lone pair, is also observed to a lesser extent in $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$, with In—Se distances of 3.468 (6) and 3.593 (6) Å. The environment of atom Tl2 has been observed previously in $\text{Tl}_2\text{Mo}_9\text{S}_{11}$ (Potel *et al.*, 1980), in which Mo_6 and Mo_{12} clusters are found, as well as in $\text{Cr}_{1.45}\text{Tl}_{1.87}\text{Mo}_{15}\text{Se}_{19}$, containing an equal mixture of Mo_6 and Mo_9 clusters (Gougeon *et al.*, 2009). In the latter compound, the Tl—Se distances range from 3.1152 (11) to 4.2214 (9) Å, compared with 2.9991 (15) to 4.0667 (9) Å in the title compound. The average Tl—Se values of 3.67 and 3.68 Å for the Tl1 and Tl2 sites, respectively, are in very good agreement with the distance of 3.68 Å expected from the sum of the ionic radii of

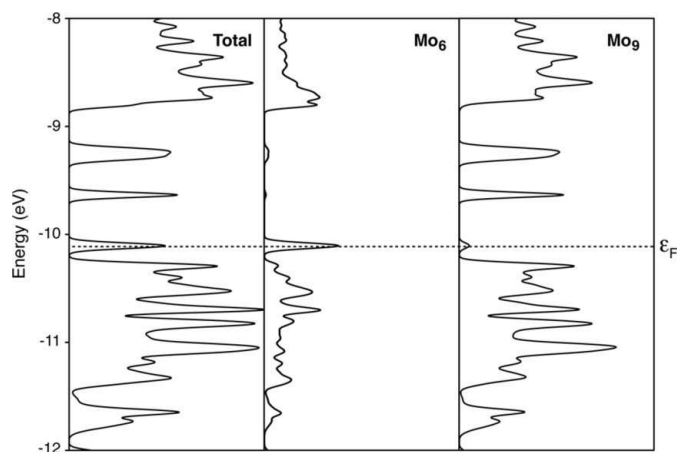


Figure 5
Total density of states computed for $(\text{Mo}_{12}\text{Se}_{15})^{4.5-}$ and projected contributions arising from Mo_6 and Mo_9 clusters.

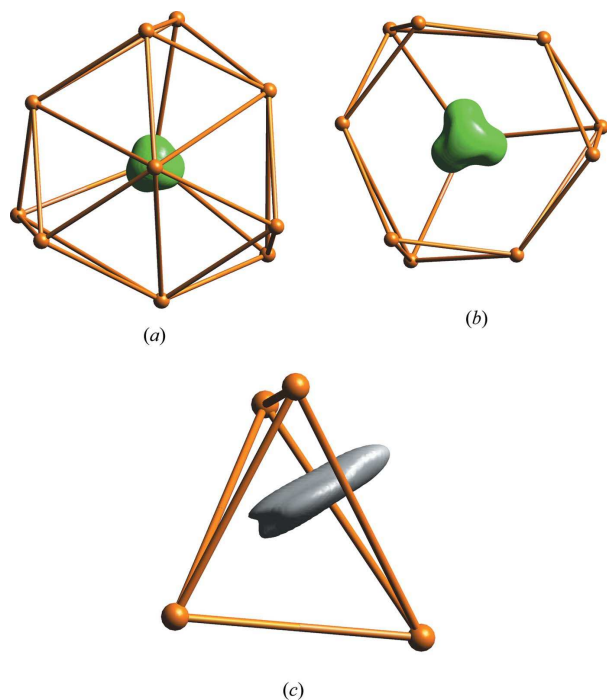


Figure 6
Nonharmonic probability density isosurfaces, viewed along the c axis, for (a) Tl1, (b) Tl2 and (c) Ag1. Se atoms are drawn at an arbitrary size. The level of the three-dimensional maps is 0.05 \AA^{-3} .

Se^{2-} and Tl^+ with coordination number 12, according to Shannon (1976).

In $\text{Rb}_{2n}(\text{Mo}_9\text{S}_{11})(\text{Mo}_{6n}\text{S}_{6n+2})$ compounds, extended Hückel tight-binding (EH-TB) calculations have shown that the clusters are hypoelectronic (Picard *et al.*, 2000). Assuming a +1 oxidation state for the Ag and Tl cations, the MEC of the whole molybdenum cluster in the title compound is 46.5. Because there are twice as many Mo_9 as Mo_6 in this compound, the MEC of one Mo_6 and two Mo_9 units is 93. EH-TB calculations have been carried out in order to check the assumption, based on distance analysis, that electrons

provided by Ag and Tl cations are uniformly distributed over both clusters. The electronic structure of the title compound is approximated by $(\text{Mo}_{12}\text{Se}_{15})^{4.5-}$. The molybdenum and selenium extended Hückel parameters used by Gautier *et al.* (1998) have been considered. The total and Mo projected density of states (DOS) curves obtained from 32 irreducible k points are sketched in Fig. 5. The Fermi level cuts a narrow peak of DOS centred on the Mo_6 cluster. This peak is derived mainly from the doubly degenerate e_g level of the molecular orbital diagram of an isolated $\text{Mo}_6\text{Se}_{14}$ cluster (Hughbanks & Hoffmann, 1983). Since this peak is roughly half-occupied, the MEC of the Mo_6 unit is close to 22 ME. The two DOS peaks that lie above the Fermi level are derived mainly from the Mo_9 cluster. These peaks show some Mo–Mo antibonding character within the bioctahedral cluster, whereas the occupied bands show an overall Mo–Mo character within the same cluster. This means that the MEC of the Mo_9 unit in this compound must be close to the optimal value. In fact, assuming an MEC of 22 for the Mo_6 cluster, the MEC per Mo_9 unit is $(93 - 22)/2 = 35.5$. This distribution differs slightly from that resulting from the analysis of Mo–Mo distances within the clusters. However, this difference cannot be considered significant since: (i) the quantum periodic calculations we have carried out are semi-empirical, (ii) Ag and Tl atoms have been neglected within the calculations because of the lack of reliable EH parameters for Tl, and (iii) the MEC values resulting from the empirical distance analysis show significant uncertainties.

Experimental

Single crystals of $\text{Ag}_{2.54}\text{Tl}_2\text{Mo}_{12}\text{Se}_{15}$ were prepared from a mixture of Ag, MoSe_2 , TlSe and Mo with the nominal composition $\text{Ag}_4\text{Tl}_2\text{Mo}_{12}\text{Se}_{14}$. Before use, Mo powder was reduced under flowing H_2 gas at 1273 K for 10 h in order to eliminate any trace of oxygen. The MoSe_2 and TlSe binaries were obtained by heating stoichiometric mixtures of the elements in sealed evacuated silica tubes for about 2 d at 1073 and 573 K, respectively. All handling of materials was carried out in an argon-filled glove-box. The initial mixture (*ca* 5 g) was cold pressed and loaded into a molybdenum crucible, which was sealed under a low argon pressure using an arc-welding system. The charge was heated at a rate of 300 K h^{-1} to 1523 K, held at that temperature for 48 h, cooled at a rate of 100 K h^{-1} to 1373 K, and finally furnace cooled.

Crystal data

$\text{Ag}_{2.535}\text{Mo}_{12}\text{Se}_{15}\text{Tl}_2$	$Z = 2$
$M_r = 3017.9$	Mo $K\alpha$ radiation
Trigonal, $P\bar{3}$	$\mu = 39.41 \text{ mm}^{-1}$
$a = 9.9962 (1) \text{ \AA}$	$T = 293 \text{ K}$
$c = 15.5364 (3) \text{ \AA}$	$0.07 \times 0.06 \times 0.03 \text{ mm}$
$V = 1344.47 (3) \text{ \AA}^3$	

Data collection

Nonius KappaCCD area-detector diffractometer	31332 measured reflections
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	5641 independent reflections
$T_{\min} = 0.104$, $T_{\max} = 0.346$	4029 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.097$

Table 1

Selected bond lengths (Å).

Mo1—Mo1 ⁱ	2.6879 (10)	Mo3—Se4	2.6466 (8)
Mo1—Mo1 ⁱⁱ	2.7007 (7)	Mo4—Mo4 ⁱⁱⁱ	2.6163 (9)
Mo1—Mo2 ⁱ	3.6041 (10)	Mo4—Mo4 ^v	3.6725 (9)
Mo1—Se1	2.5914 (8)	Mo4—Se3	2.6791 (9)
Mo1—Se1 ⁱ	2.6193 (8)	Mo4—Se4	2.5688 (8)
Mo1—Se1 ⁱⁱ	2.5741 (9)	Mo4—Se4 ⁱⁱⁱ	2.6637 (8)
Mo1—Se2 ⁱ	2.6457 (11)	Mo4—Se4 ^{vi}	2.6520 (12)
Mo1—Se5	2.5492 (9)	Mo4—Se7	2.5795 (9)
Mo2—Mo2 ⁱⁱⁱ	2.6374 (8)	Tl2—Tl2 ^{vii}	3.2831 (17)
Mo2—Mo3	2.6896 (8)	Ag1—Se2 ⁱ	2.6675 (17)
Mo2—Mo3 ⁱⁱⁱ	2.7757 (7)	Ag1—Se3	2.577 (2)
Mo2—Se1	2.7085 (10)	Ag1—Se4 ⁱ	2.6834 (16)
Mo2—Se2	2.6523 (8)	Ag1—Se7 ^v	3.0215 (17)
Mo2—Se2 ⁱⁱⁱ	2.5787 (8)	Tl1—Se1 ^{viii}	3.6179 (8)
Mo2—Se3	2.6652 (9)	Tl1—Se2 ^{ix}	3.3036 (8)
Mo2—Se6	2.5319 (9)	Tl1—Se3 ⁱⁱⁱ	4.2039 (9)
Mo3—Mo3 ⁱⁱⁱ	2.7346 (7)	Tl1—Se6	3.0677 (14)
Mo3—Mo4	2.7475 (8)	Tl1—Se7 ^x	3.8863 (14)
Mo3—Mo4 ^{iv}	2.6628 (8)	Tl2—Se3 ^{xi}	3.7544 (7)
Mo3—Se2	2.6275 (7)	Tl2—Se4 ^{xii}	3.4181 (7)
Mo3—Se3	2.5765 (11)	Tl2—Se4 ^{xiii}	4.0667 (9)
Mo3—Se3 ^{iv}	2.5839 (13)	Tl2—Se5 ^{xi}	2.9991 (15)

Symmetry codes: (i) $-x + y, -x, z$; (ii) $y, -x + y, -z - 1$; (iii) $-y - 1, x - y - 1, z$; (iv) $-x + y, -x - 1, z$; (v) $-x - 1, -y - 1, -z$; (vi) $y, -x + y, -z$; (vii) $-x + 2, -y + 2, -z + 2$; (viii) $x - y, x, -z - 1$; (ix) $-x, -y - 1, -z - 1$; (x) $x, y, z - 1$; (xi) $x + 1, y + 1, z + 1$; (xii) $-y + 1, x - y + 1, z + 1$; (xiii) $y + 1, -x + y + 1, -z + 1$.

Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.048$$

$$wR(F^2) = 0.079$$

$$S = 1.28$$

5641 reflections

143 parameters

$$\Delta\rho_{\max} = 3.78 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -2.71 \text{ e } \text{\AA}^{-3}$$

The structure was solved in the space group $P\bar{3}$ using *SIR97* (Altomare *et al.*, 1999), which revealed all atoms. The final model was refined down to $R = 0.169$. Analysis of the data with the TwinRotMat procedure implemented in *PLATON* (Spek, 2009) revealed that the crystal investigated was merohedrally twinned. Introduction of the twinning matrix (010, 100, 00 $\bar{1}$) lowered the R factor to 0.059. At this stage, the difference Fourier map revealed significant electron densities near atoms Tl1 (5.10 and $-2.45 \text{ e } \text{\AA}^{-3}$), Tl2 (7.75 and $-8.06 \text{ e } \text{\AA}^{-3}$) and Ag1 (5.59 and $-3.85 \text{ e } \text{\AA}^{-3}$). Fourth-order tensors in the Gram–Charlier expansion (Johnson & Levy, 1974) of the thallium and silver displacement parameters were used to better describe the electron density around these cationic sites. The residual R value dropped to 0.0476 and the residual peaks in the vicinity of Tl1 to 3.50 and $-1.64 \text{ e } \text{\AA}^{-3}$, in the vicinity of Tl2 to 2.87 and $-1.72 \text{ e } \text{\AA}^{-3}$, and in the vicinity of Ag1 to 2.05 and $-1.95 \text{ e } \text{\AA}^{-3}$. The nonharmonic probability density function maps of Tl1, Tl2 and Ag1 did not show significant negative regions, indicating that the refined model can be considered valid (Bachmann & Schulz, 1984). Fig. 6 shows the isosurfaces of the probability density for the Ag and Tl atoms. The twin volume ratio was refined to 0.338 (1):0.662 (1). Refinement of the occupancy factor of atom Ag1 led to the final stoichiometry $\text{Ag}_{2.535(9)}\text{Ti}_2\text{Mo}_{12}\text{Se}_{15}$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *EVALCCD* (Duisenberg, 1998); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999);

program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *JANA2006*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3050). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Bachmann, R. & Schulz, H. (1984). *Acta Cryst.* **A40**, 668–675.
- Bars, O., Guillevis, J. & Grandjean, D. (1973). *J. Solid State Chem.* **6**, 48–57.
- Brandenburg, K. (2001). *DIAMOND*. Version 2.1e. Crystal Impact GbR, Bonn, Germany.
- Cava, R. J., Santoro, A. & Tarascon, J. M. (1984). *J. Solid State Chem.* **54**, 193–203.
- Duisenberg, A. J. M. (1998). PhD thesis, University of Utrecht, The Netherlands.
- Gautier, R., Gougeon, P., Halet, J.-F., Potel, M. & Saillard, J.-Y. (1997). *J. Alloys Compd.* **262–263**, 311–315.
- Gautier, R., Picard, S., Gougeon, P. & Potel, M. (1998). *Mater. Res. Bull.* **34**, 93–101.
- Gougeon, P. (1984). PhD thesis, University of Rennes, France.
- Gougeon, P., Padiou, J., Le Marouille, J.-Y., Potel, M. & Sergent, M. (1984). *J. Solid State Chem.* **51**, 218–226.
- Gougeon, P., Potel, M. & Gautier, R. (2004). *Inorg. Chem.* **43**, 1257–1263.
- Gougeon, P., Potel, M., Padiou, J. & Sergent, M. (1987). *Mater. Res. Bull.* **22**, 1087–1093.
- Gougeon, P., Potel, M., Padiou, J. & Sergent, M. (1988). *Mater. Res. Bull.* **23**, 453–460.
- Gougeon, P., Potel, M. & Sergent, M. (1989a). *Acta Cryst.* **C45**, 182–185.
- Gougeon, P., Potel, M. & Sergent, M. (1989b). *Acta Cryst.* **C45**, 1413–1415.
- Gougeon, P., Potel, M. & Sergent, M. (1989c). *Acta Cryst.* **C45**, 1285–1287.
- Gougeon, P., Potel, M. & Sergent, M. (1990). *Acta Cryst.* **C46**, 2284–2287.
- Gougeon, P., Salloum, D. & Potel, M. (2009). *Acta Cryst.* **C65**, i87–i90.
- Hughbanks, T. & Hoffmann, R. (1983). *J. Am. Chem. Soc.* **105**, 1150–1162.
- Johnson, C. K. & Levy, H. A. (1974). *International Tables for X-ray Crystallography*, edited by J. A. Ibers & W. C. Hamilton, Vol. IV, pp. 311–336. Birmingham: Kynoch Press.
- Le Berre, F., Hamard, C., Pena, O. & Wojakowski, A. (2000). *Inorg. Chem.* **39**, 1100–1105.
- Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Petříček, V., Dušek, M. & Palatinus, L. (2006). *JANA2006*. Institute of Physics, Prague, Czech Republic.
- Picard, S., Gougeon, P. & Potel, M. (1999). *Angew. Chem. Int. Ed.* **38**, 2036.
- Picard, S., Gougeon, P. & Potel, M. (2001). *Acta Cryst.* **C57**, 335–336.
- Picard, S., Halet, J.-F., Gougeon, P. & Potel, M. (1999). *Inorg. Chem.* **38**, 4422–4429.
- Picard, S., Saillard, J.-Y., Gougeon, P., Noel, H. & Potel, M. (2000). *J. Solid State Chem.* **155**, 417–426.
- Potel, M., Chevrel, R. & Sergent, M. (1980). *Acta Cryst.* **B36**, 1319–1322.
- Potel, M., Chevrel, R. & Sergent, M. (1981). *Acta Cryst.* **B37**, 1007–1010.
- Potel, M., Gougeon, P., Chevrel, R. & Sergent, M. (1984). *Rev. Chim. Miner.* **21**, 509–536.
- Schäfer, H. & von Schnering, H. G. (1964). *Angew. Chem.* **76**, 833–849.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Thomas, C., Picard, S., Gautier, R., Gougeon, P. & Potel, M. (1997). *J. Alloys Compd.* **262–263**, 305–310.
- Tortelier, J. & Gougeon, P. (1998). *Inorg. Chem.* **37**, 6229–6236.
- Yvon, K., Paoli, A., Flükiger, R. & Chevrel, R. (1977). *Acta Cryst.* **B33**, 3066–3072.